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(21) International Application Number: PCT/CA97/00003 (22) International Filing Date: 3 January 1997 (03.01.97) (30) Priority Data: 08/583,638 5 January 1996 (05.01.96) US (71) Applicant (for all designated States except US): BALLARD POWER SYSTEMS INC. [CA/CA]; 9000 Glenlyon Parkway, Burnaby, British Columbia V5J 5J9 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): STECK, Alfred, E. [CA/CA]; 3956 Westridge Avenue, West Vancouver, British Columbia V7V 3H7 (CA). STONE, Charles [CA/CA]; 411 - 237 E. 4th Avenue, Vancouver, British Columbia V5T 4R4 (CA). (74) Agent: RUSSELL REYNEKE; Suite 700, Two Bentall Centre, 555 Burrard Street, Vancouver, British Columbia V7X 1M8 (CA).		(81) Designated States: AU, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims and statement.</i> Date of publication of the amended claims and statement: 12 September 1997 (12.09.97)
(54) Title: α,β,β -TRIFLUOROSTYRENE-BASED AND SUBSTITUTED α,β,β -TRIFLUOROSTYRENE-BASED COMPOSITE MEMBRANES (57) Abstract A composite membrane is provided in which a porous substrate is impregnated with a polymeric composition comprising various combinations of α,β,β -trifluorostyrene, substituted α,β,β -trifluorostyrene and ethylene-based monomeric units. Where the polymeric composition includes ion-exchange moieties, the resultant composite membranes are useful in electrochemical applications, particularly as membrane electrolytes in electrochemical fuel cells.		

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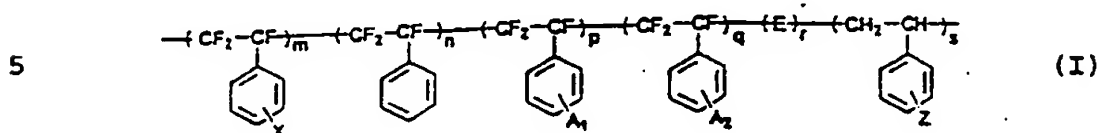
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AMENDED CLAIMS

[received by the International Bureau on 17 July 1997 (17.07.97);
original claims 1-82 replaced by new claims 1-20 (5 pages)]

1. A composite membrane comprising a porous sheet material impregnated with a polymer consisting predominantly of fragments of formula (I):



wherein m, n, p, q, r, and s are zero or an integer greater than zero, and at least one of m, n, p and q is an integer greater than zero;

X is selected from the group consisting of
10 SO₂F, SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, OPO₃H₂, OArSO₃H where Ar is an aryl, NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group consisting of
15 alkyls, perfluoroalkyls and aryls);

A₁ and A₂ are selected from the group consisting of halogens, C_xH_yF_z (where x is an integer greater than zero and y+z = 2x+1), CF=CF₂, CN, NO₂ and OH, O-R (where R is selected from the
20 group consisting of alkyls and perfluoroalkyls and aryls), and when m is an integer greater than zero, the group from which A₁ and A₂ are selected further consists of SO₂F, SO₃H, PO₂H₂, PO₃H₂, CH₂PO₃H₂, COOH, OSO₃H, OPO₂H₂, OPO₃H₂, OArSO₃H where
25 Ar is an aryl, NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH₂NR₃⁺ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls);

30 Z is selected from the group consisting of hydrogen, fluorine, C_xH_yF_z (where x is an integer

greater than zero and $y+z = 2x+1$), SO_2F , SO_3H ,
 PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 ,
 OArSO_3H where Ar is an aryl, NR_3^+ (where R is
selected from the group consisting of alkyls,
5 perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is
selected from the group consisting of alkyls,
perfluoroalkyls and aryls); and

E is selected from the group consisting of
 CH_2-CH_2 , CH_2-CHF , $\text{CFH}-\text{CFH}$, CF_2-CH_2 , CF_2-CHF , CF_2-CF_2 .

10 2. The composite membrane of claim 1
 wherein p is an integer greater than zero.

 3. The composite membrane of claim 1
 wherein m is an integer greater than zero.

15 4. The composite membrane of claim 3
 wherein at least one of n, p and q is an integer
 greater than zero.

 5. The composite membrane of claim 3
 wherein at least one of p and q is an integer
 greater than zero.

20 6. The composite membrane of claim 3
 wherein X is SO_2F .

 7. The composite membrane of claim 6
 wherein at least one of n, p and q is an integer
 greater than zero.

25 8. The composite membrane of claim 6
 wherein n and p are integers greater than zero,
 and A_1 is selected from the group consisting of
 fluorine, CF_3 , and para-phenoxy.

9. The composite membrane of claim 3 wherein X is SO_3H and n is an integer greater than zero.

10. The composite membrane of claim 9
5 wherein at least one of p and q is an integer greater than zero.

11. The composite membrane of claim 10 wherein p is an integer greater than zero, and A_1 is selected from the group consisting of fluorine, CF₃, and para-phenoxy.
10

12. The composite membrane of claim 3 wherein p is an integer greater than zero, and A_1 is selected from the group consisting of SO_2F , SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_3H_2 , OPO_3H_2 , OArSO_3H where Ar is an aryl, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).
15

13. The composite membrane of claim 1 wherein said porous sheet material is a polymeric sheet material.

14. The composite membrane of claim 13 wherein said porous polymeric sheet material comprises polytetrafluorethylene.

15. The composite membrane of claim 13 wherein said porous polymeric sheet material comprises a polyolefin.

16. The composite membrane of claim 13

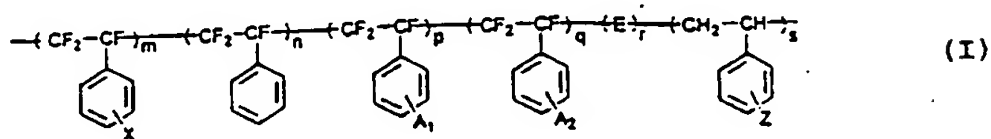
wherein said porous polymeric sheet material comprises a partially fluorinated polyolefin.

17. The composite membrane of claim 13 wherein said porous polymeric sheet material comprises a polymer selected from the group consisting of polyethylene, polypropylene, polyvinylidene fluoride, poly(ethylene-co-tetrafluoroethylene) and poly(tetrafluoroethylene-co-hexafluoropropylene).

18. The composite membrane as in any of claims 1-14, wherein said porous sheet material is expanded polytetrafluoroethylene film.

19. The composite membrane as in any of claims 1-17 wherein said composite membrane is substantially gas impermeable.

20. A composite membrane comprising a porous sheet material impregnated with a polymer consisting essentially of fragments of formula (I):



wherein m, n, p, q, r, and s are zero or an integer greater than zero, and at least one of m, n, p and q is an integer greater than zero;

X is selected from the group consisting of SO_2F , SO_3H , PO_2H_2 , PO_3H_2 , $\text{CH}_2\text{PO}_3\text{H}_2$, COOH , OSO_3H , OPO_2H_2 , OPO_3H_2 , OArSO_3H where Ar is an aryl, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and CH_2NR_3^+ .

(where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls);

A_1 and A_2 are selected from the group consisting of halogens, $C_xH_yF_z$ (where x is an integer greater than zero and $y+z = 2x+1$), $CF=CF_2$, CN, NO_2 and OH, O-R (where R is selected from the group consisting of alkyls and perfluoroalkyls and aryls), and when m is an integer greater than zero, the group from which A_1 and A_2 are selected further consists of SO_2F , SO_3H , PO_2H_2 , PO_3H_2 , $CH_2PO_3H_2$, COOH, OSO_3H , OPO_2H_2 , OPO_3H_2 , $OArSO_3H$ where Ar is an aryl, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls);

Z is selected from the group consisting of hydrogen, fluorine, $C_xH_yF_z$ (where x is an integer greater than zero and $y+z = 2x+1$), SO_2F , SO_3H , PO_2H_2 , PO_3H_2 , $CH_2PO_3H_2$, COOH, OSO_3H , OPO_2H_2 , OPO_3H_2 , $OArSO_3H$ where Ar is an aryl, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); and

E is selected from the group consisting of CH_2-CH_2 , CH_2-CHF , $CFH-CFH$, CF_2-CH_2 , CF_2-CHF , CF_2-CF_2 .

STATEMENT UNDER ARTICLE 19

The number of claims in the present application has been reduced from 82 to 20, and the number of independent claims has been reduced from 29 to only two. New claim 1 is a broad generic claim which recites in one claim the limitations of former independent claims. All of the other pending claims depend from new claim 1, with the exception of new claim 20. New claim 20 is identical to new claim 1, but employs "consisting essentially of" instead of "comprising" terminology.

New claims 1-20 are supported in the specification at page 5, line 23 - page 19, line 9 (Summary Of The Invention). Specifically, embodiments of formula (I) wherein one or more of m, n, p and q are an integer greater than zero are disclosed in the specification at page 5, line 23 - page 6, line 6, page 8, line 1 - page 11 line 29, and page 15, line 20 - page 17, line 20. Copolymers of α,β,β -trifluorostyrene and/or substituted α,β,β -trifluorostyrene incorporating fragments denoted by "E" (that is, embodiments of formula (I) wherein r is also an integer greater than zero), are disclosed in the specification at page 6, lines 3-27 and page 13, line 21 - page 14, line 6. Copolymers of α,β,β -trifluorostyrene and/or substituted α,β,β -trifluorostyrene incorporating styrene-based fragments (that is, embodiments of formula (I) wherein s is also an integer greater than zero), are disclosed in the specification at page 7, lines 13-30 and page 14, line 24 - page 15, line 9.